Surface Charge Characteristics of Some Acid Soils of Sri Lanka

P. LOGANATHAN AND T. W. FERNANDO

Coconut Research Institute, Lunuwila, Sri Lanka

SUMMARY

Surface charge characteristics of 14 samples belonging to three Great Soil Groups, Ultisol, Alfisol and Entisol, at different pH and ionic strengths showed that soils contain predominantly the "constant surface potential" type of colloids; the Alfisols contain also some colloids of the "constant surface charge" type. The point of zero charge of the soils ranged from pH 3.0 to 4.3 with the Alfisols having the lowest values and the Ultisols the highest. Net surface charge densities at the soil pH and pH 7.0 and ionic strengths of 0.005 M and 1 M showed that cation exchange capacity as determined by the routine NH_4OAc method may give very unrealistic values compared to the actual field situation.

Addition of phosphorus decreased the point of zero charge and increased the negative surface charge densities of these soils.

INTRODUCTION

Surface charge characteristics of soil colloids are responsible for various important physico-chemical properties such as ion exchange, ion mobility, aggregate stability, erosivity etc. The difference in behaviour of tropical soils from temperate soils with respect to these properties is often due to their basic differences in the surface charge characteristics. Soils of the temperate region are mainly of the constant surface charge type, where the charges arise from isomorphous substitution in the 2:1 clays, whereas the soils of the humid tropics are of the constant potential type where the charges arise from the ionisation of hydroxyls of the 1:1 clays and hydrous oxides. The Gouy-Chapman theory of the electrical double layer predicts that the charges of the constant potential type of colloids vary markedly with pH, electrolyte concentration and valence of counter ions and therefore routine measurements of cation exchange or anion exchange capacities used in the temperate countries are of doubtful value when applied to tropical soils. Studies reported on Oxisols and Inceptisols from Hawaii (El-Swaify and Sayegh, 1975) on Oxisols, Alfisols (van Raij and Peech, 1972; Ilton Morais *et al.*, 1976) and Ultisols (Ilton Morais *et al.*, 1976) from Brazil and on Alfisols and Ultisols from Nigeria (Gallez *et al.*, 1976) showed that the surface charge characteristics of the humid tropical soils are distinctly different from those of the temperate soils.

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As there is no information on the surface charge characteristics of Sri Lanka soils and their dependence on pH, ionic strength and the nature of ions in the ambient solution, this study was undertaken. This paper presents data on these aspects for some of the important coconut growing acid soils belonging to the Great Soil Groups, Ultisol, Alfisol and Entisol.

MATERIALS AND METHODS

Seven soils belonging to three Great Soil Groups, Ultisol, Alfisol and Entisol were selected from the Intermediate and Wet rainfall zones of the coconut-growing regions. Surface and sub surface soil samples were collected from the fertilized area in close proximity to coconut palms and unfertilized area at the centre of square formed by 4 palms. They were air dried and ground to pass through 2 mm sieve. Some relevant properties of the soil samples are shown in Table 1.

Point of zero charge (PZC) by ΔpH method

Three gm soil samples were placed in 25 ml beakers and pH values were adjusted with HCI or NaOH to cover the expected PZC. The final volume of the suspensions was made to 20 ml. After 2days of equilibrium with intermittant stirring within a constant humidity chamber, pH values were recorded, 0.5 ml of 2 M NaCl added and pH values were re-recorded after 3 hours of frequent stirring. The pH in at which ΔpH = O is the PZC and this was obtained from a plot of ΔpH vs pH in H_2O.

pH was measured using a Corning Expandometric pH meter with a combination glass and calomel electrodes.

Potentiometric titrations

A series of 5 gm acid washed soil samples were equilibrated with known amounts of acid (HCI) and base (NaOH) in various concentrations of NaCl for 2 days in a closed humidified chamber to prevent evaporation. The pH was determined at the end of this period. The amounts of H^4/OH^- ions adsorbed at a given pH value is equal to the amount of HC1 and NaOH added after correction for the amount of acid or base required to bring the electrolyte solution alone to the same pH value. The net surface charge is plotted against equilibrium pH for all ionic strengths. According to Gouy-Chapman's double layer theory, the point where these curves interesect is the PZC.

RESULTS ND DISCUSSION

Potentiometric titration curves at different ionic strengths for three samples-one each belonging to Ultisol, Alfisol and Entisol-are shown in Figures 1 to 3. The other samples in each of these Great Soil Groups behaved in a similar manner. The charge–pH curves measured in the various ionic strengths

Table 1—Classification and selected properties of the soils

Soils	*Classification*	*Depth (cm)*	*Treatment*	*Sand %*	*Silt %*	*Clay %*	*pH (1:5 H_2O)*	*1M NH_4 OAc pH=7 CEC me/g*	*Organic carbon %*	*Free oxide %*
Naiwala	Ultisol	0–15	Unfertilized	58.6	5.9	29.4	4.9	0.074	1.73	1.33
	(Red yellow Podzolic)	25–40	—do—	50.8	4.7	35.9	4.9	0.060	2.14	1.85
		0–15	Fertilized	59.0	7.7	25.6	5.9	0.094	1.94	1.45
		25–40	—do—	58.6	10.2	30.2	4.5	0.085	1.19	1.68
Bandirippuwa	—do—	0–15	Unfertilized	73.7	3.8	13.5	5.0	0.042	1.28	1.51
		25–40	—do—	74.2	3.3	20.7	4.9	0.031	2.80	2.10
Alubomulla	—do—	0–50	—do—	67.7	3.8	23.0	4.4	0.140	2.24	1.71
Halmillakotuwa	Alfisol	0–15	—do—	74.1	7.5	15.6	6.3	0.079	0.76	2.31
	(Reddish Brown Earth)	25–40	—do—	67.1	6.5	22.2	6.3	0.077	0.51	2.73
Indihena	Alfisol	0–15	—do—	89.3	3.9	5.9	5.9	0.044	0.51	0.17
	(Non Calcic Brown)	25–40	—do—	88.7	2.1	7.4	5.8	0.035	0.39	0.21
Keenakelle	Entisol (Regosol)	0–15	—do—	86.6	3.0	9.3	5.9	0.030	0.57	0.84
		25–40	—do—	81.3	3.2	14.8	5.5	0.036	0.44	1.19
Waikkala	—do—	0–50	—do—	88.5	2.0	8.1	4.7	0.033	0.47	1.01

intersected one another at single points indicating that these soils belong to the constant potential type of colloids with H^4+ and OH^- as the potential determining ions. In the case of Entisols (Figute 3) the curves for any two ionic strengths converged or intersected at pH 6, in addition to the PZC around pH 3.5 Gallez *et al.* (1976) also reported similar results for a Nigerian soil and a kaolinite of recent formation. They explained that in kaolinites of recent formation, the interaction of kaolinite edge surface and iron oxides had not advanced to a greater degree to give a single PZC which is that of the kaolinite-iron oxide system after complete interaction. This explanation may also apply to the case of the Entisols as they are of recent formation.

The charge–pH curves for all samples show that at any pH, increase of ionic strength increases the surface charge as predicted by the Gouy-Chapman double layer theory for constant potential type of colloids.

The PZC values obtained from the potentiometric titration method for the Ultisols and Alfisols ranged between 3.0 to 3.8 (Table 2). These values agreed fairly well with those determined by the ΔpH method and values of around 3.5 for Alfisols and 4.0 for Ultisols reported for Nigerian soils (Gallez *et al*, 1976) and values of 3.4 to 3.8 for Alfisols of Brazil (van Raij and Peech, 1972).

Table 2—Zero point of charge and effect of ionic strength on the net surface charge of the soils

Soils (Unfertilized)	*Depth (cm)*	*PZC ΔpH method*	*PZC potentio metric method*	*Net charge at soil pH (me/g) I=0.005 M*	*Net charge at soil pH (me/g) I=1 M*	*Net charge at pH=7 (me/g) I=0.005M*	*Net charge at pH=7 (me/g) I=1M*
Naiwala	0–15	3.6	3.8	–0.019	–0.040	–0.069	–0.120
	25–40	3.6	3.7	–0.018	–0.035	–0.073	–0.120
Bandirippuwa	0–15	4.3	3.4	–0.015	–0.025	–0.040	–0.063
	25–40	4.2	3.5	–0.013	–0.023	–0.032	–0.057
Halmillakotuwa	0–15	3.6	3.4	–0.048	–0.071	–0.071	–0.098
	25–40	3.5	3.5	–0.044	–0.060	–0.058	–0.083
Indihena	0–15	3.9	3.1	–0.020	–0.026	–0.026	–0.045
	25–40	3.8	3.0	–0.023	–0.038	–0.032	–0.054
Keenakelle	0–15	3.7	3.4	–0.023	–0.028	–0.034	–0.039
	25–40	3.8	3.5	–0.025	–0.029	–0.038	–0.044
Waikkala	0–50	3.8	4.2	–0.004	–0.009	–0.020	–0.029

The low PZC may be attributed to the presence of predominantly kaolinitic type of minerals in these soils. Among the soils studied Alfisols had the lowest PZC. This is probably due to the presence of some 2:1 minerals in these soils (De Alwis and Pannaboke, 1972-73) which is expected to have permanent negative charges. The PZC in these soils is far to the acid side of the zero point of titration (where equal quantities of H^4+ and OH^- were added) indicating the presence of permanent negative charges (van Raij and Peech, 1972).

Table 2 gives the net surface charge densities at the field pH and ionic strength of the soils and at the conditions of the routine laboratory measurements of cation exchange capacity. The results show that for Ultisols the net surface charge at ionic strength $1M$ and pH 7 is about 4 to 6 times higher than that under field conditions and for Entisols and Alfisols it is about 2 times higher. Therefore the cation exchange capacity determined by 1 M NH_4 OAc at pH 7 and exchange acidity by 1 M Ba Cl_2 pH 8 may result in extremely high values. During the determination of cation exchange capacity the soil is washed with alcohol to remove the excess salts and thereby the ionic strength is lowered. This reduces the charge on the surface and desorbs some of the adsorbed ions. This is probably one of the main reasons for the lower cation exchange capacity values by NH_4 OAc method (Table 1) relative to the net negative charge density values at pH 7 and ionic strength $1M$ (Table 2). A more realistic method of determination of cation exchange capacity is to use a dilute electrolyte with concentrations similar to those in the field soil solution or by the determination of exchangeable bases and "H+Al" by dilute unbuffered extractants (van Raij and Peech, 1972; Gallez *et al.*, 1976).

For Alfisols, the effects of pH and ionic strength were not strikingly high as in the case of Ultisols. This is probably due to the presence of some constant surface charge type of colloids in addition to the constant potential type in the Alfisols-the charges of the former type are not affected by pH and ionic strength.

Addition of phosphate to Alubomulla decreased the PZC from 4.0 to 3.7 and increased the net negative charge (Table 3 and Figure 4). These effects are due to the specific adsorption of phosphate. Specifically adsorbing anions shift the PZC to the acid side and cations to the alkaline side (Hingston *et al.*, 1967). Indifferent electrolytes have no effect on the PZC. Reduction of PZC on addition of phosphate to an Inceptisol and an Oxisol from Hawaii was reported by EI-Swaify and Sayegh (1975). The degree of reduction depends on the amount of phosphate added per gm of soil. A sample collected from a rock phosphate treated area in a long term fertilizer experiment showed a PZC lower than the sample from the unfertilized area and negative charges about 4 times higher (Table 3 and Figure 5). This is most likely due to the specific adsorption of the phosphate ions in the soils of the fertilized area. The cation exchange capacity measured with $1M$ NH_4 OAc, pH 7 is also higher in the fertilized area (Table).1

Table 3—**Effect of phosphate treatment on PZC and net surface charge**

Soil	*Depth* (cm)	*Treatment*	*PZC*	*Net charge at soil pH and* I=0.005 M (*me*/g)
Alubomulla	0–50	–P	4.0	–0.005
	0–50	+P	3.7	–0.020
Naiwala	0–15	–P	3.8	–0.006
	0–15	+P	3.4	–0.028

It was reported for some soils that the surface layers had very much lower PZC than the subsoil and attributed this to the presence of higher amounts of organic matter in the surface soils, which tend to lower the PZC (van Raij and Peech, 1972; Ilton Marais *et al.*, 1976). In contrast, the soils studied here had no such marked differences in PZC (Table 2) perhaps due to the presence of nearly equal contents of organic matter in the surface and sub soils (Table 1).

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Figure Captions

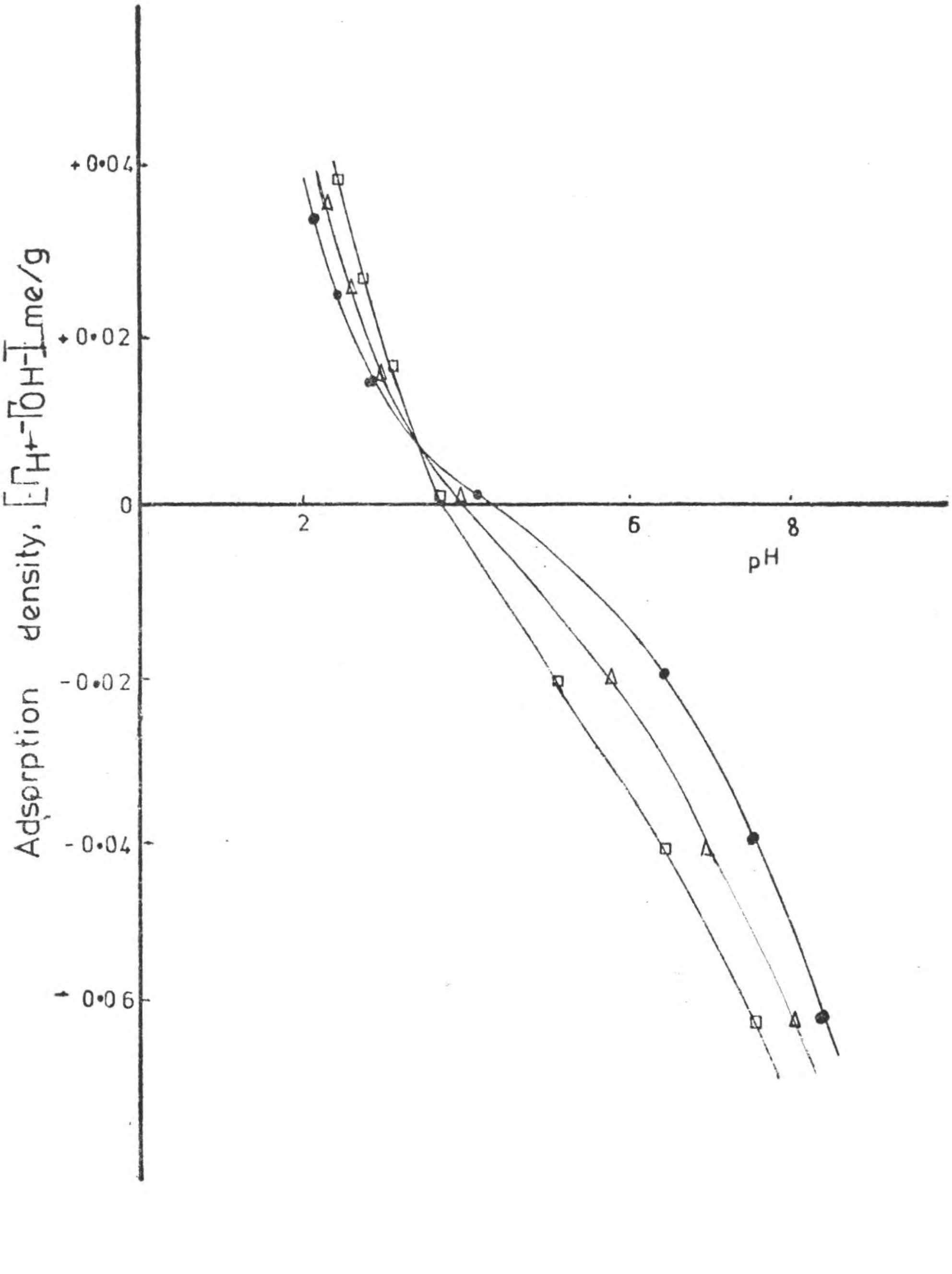
Figure 1 Surface charge–pH curves of Bandirippuwa soil (25-40 cm). ●–0.005 M NaCl.; △ –0.050 M NaCl; □ –0.500 M NaCl.

Figure 2. Surface charge pH curves of Halmillakotuwa soil, 25-40 cm). ●–0.005 M NaCl: △ –0.050 M NaCl; ×–0.500 M Nacl.

Figure 3. Surface charge–pH curves of Keenakelle soil (25-40 cm). ●–0.005 M NaCl; △–0.050 M NaCl; ×–0.200 M Nacl; □ –0.500 M Nacl.

Figure 4. Surface charge–pH curves of Alubomulla soil .0.50 cm). ●–0.0015 M NaCl; △–0.0150 M NaCl; □ –0.1500 M NaCl. Solicd lines without P, dotted lines– with P.

Figure 5. Surface charge–pH curves of Naiwala soil (0.15cm). ●–0.005 M NaCl; △ –0.050 M NaCl; □ –0.200 M NaCl. Solid lines–without P, dotted lines–with P.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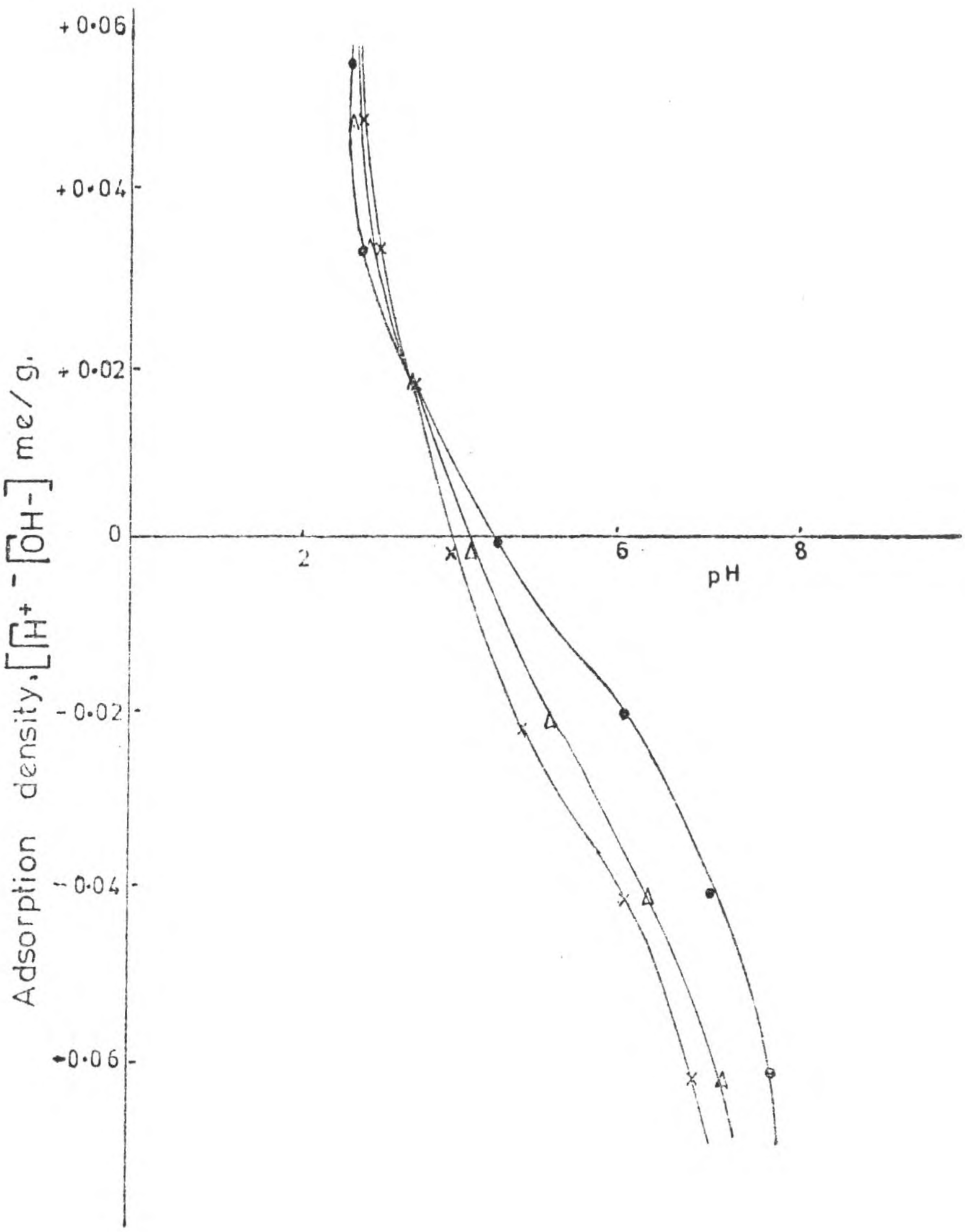
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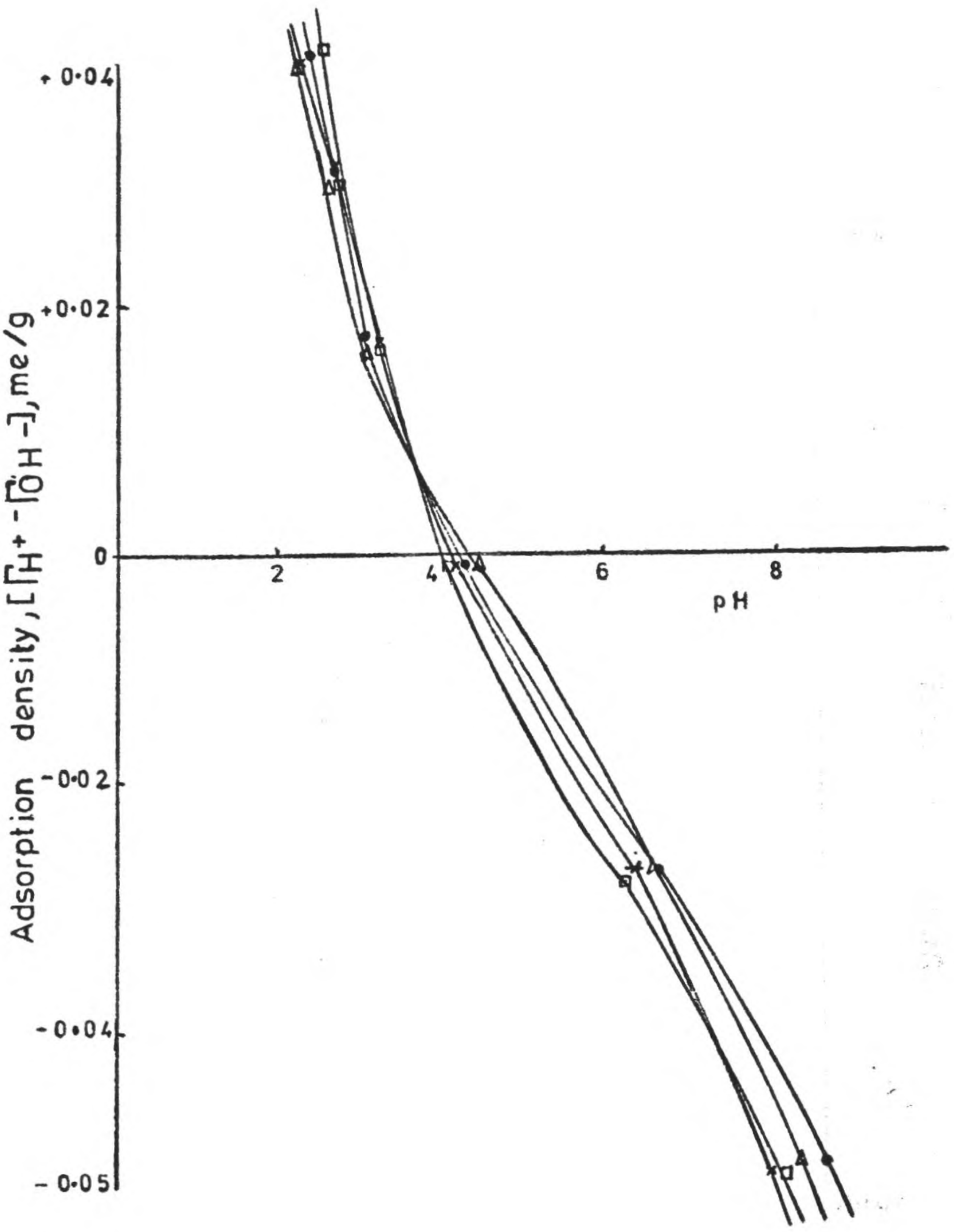
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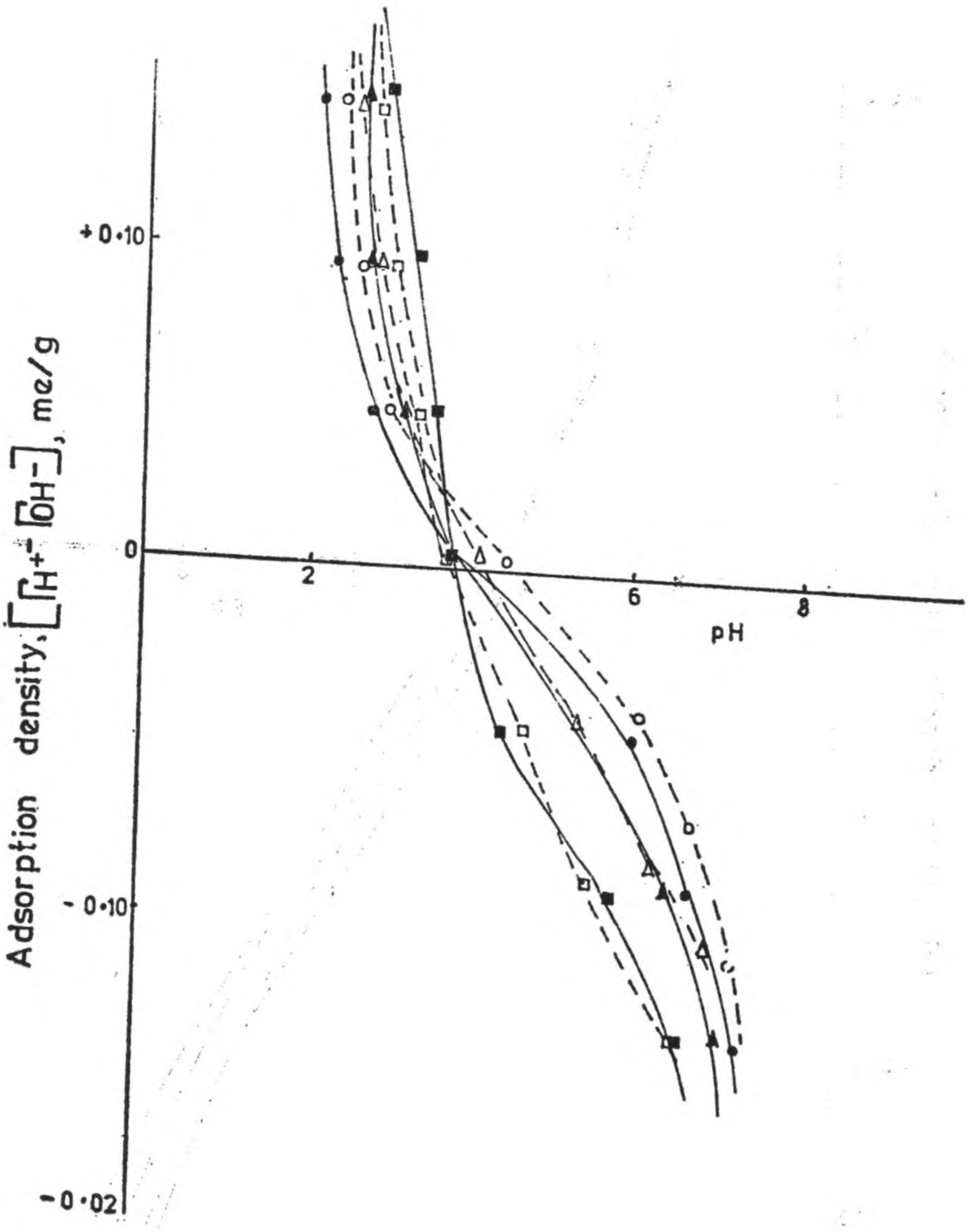
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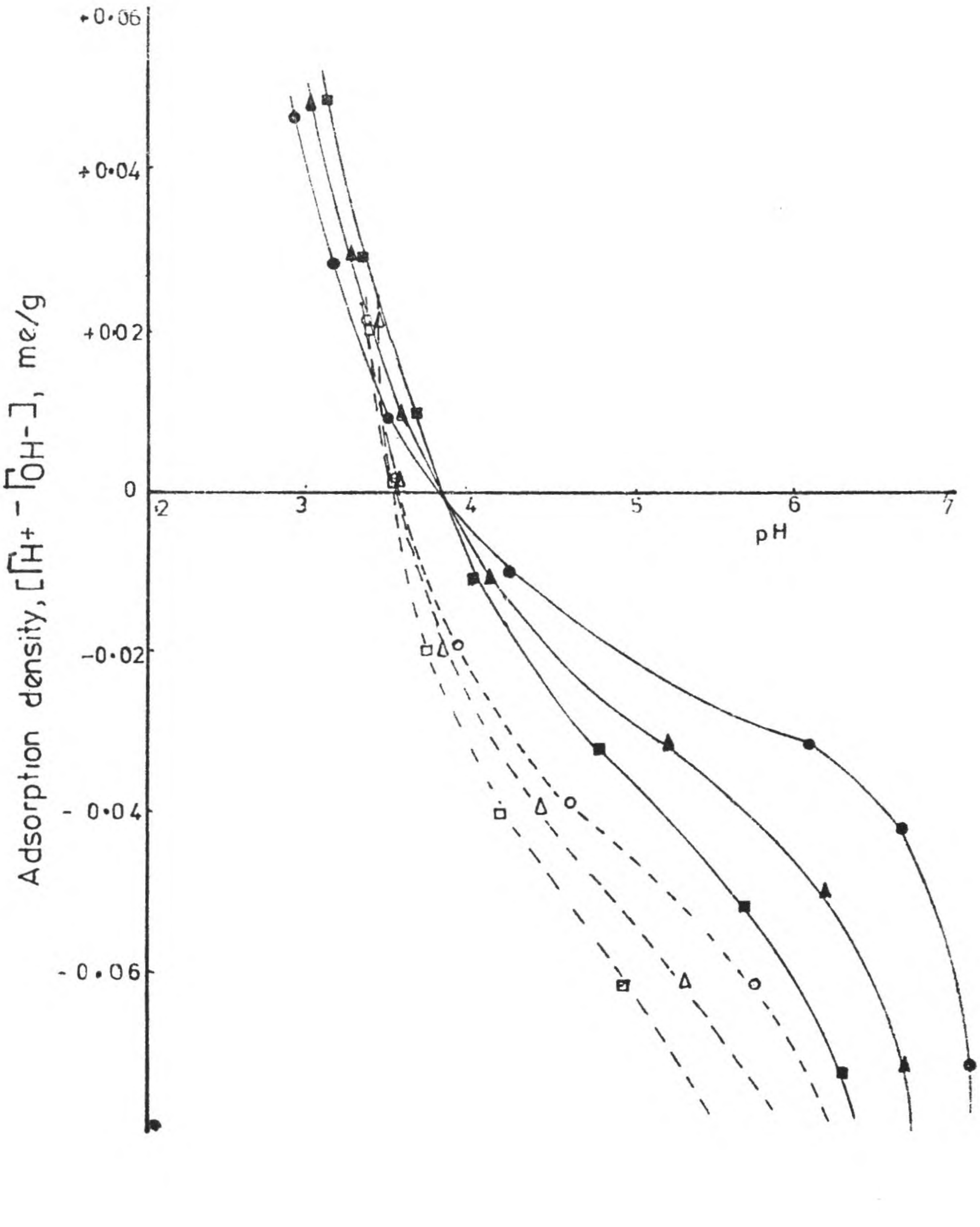
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